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Trans-cis ISOMERIZATION OF DIMETHYLBIS(DIETHYLPHENYLPHOSPHINE)PALLADIUM(II) CATALYZED BY METHYLMAGNESIUM COMPOUNDS *

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Summary

Dimethylbis(diethylphenylphosphine)palladium(II) complex was found to undergo a facile *trans-cis* isomerization reaction in tetrahydrofuran containing methylmagnesium compounds such as Me_2Mg and MeMgBr. Kinetic and isotopic studies on the isomerization process suggest the occurrence of methylmagnesium-catalyzed isomerization through an intermolecular methyl exchange process between methylpalladium and methylmagnesium compounds involving a partial dissociation of phosphine ligand.

Introduction

In contrast to numerous reports concerning the *trans-cis* isomerization mechanisms of inorganic square planar complexes of d^8 transition metals [1], studies on the isomerization reactions of corresponding square planar organometallic compounds are still scarce [2,3]. Information on the isomerization processes of organometallic complexes is of fundamental importance for understanding chemical properties of organometallic complexes. The two most important concerted thermolysis pathways of dialkyl-transition metal complexes relevant to organic synthesis are reductive elimination and β-elimination; the former process affords C–C coupling products while the latter generates alkenes and alkanes. Thus information regarding the controlling factors on the two processes is critical for achieving selective metal-promoted organic synthesis. The course of thermolysis pathways in decomposition of some dialkylpalladium complexes has been found to be dictated by their geometries in the square planar configurations as best illustrated in thermolysis of

* This paper is dedicated to Jack Halpern to celebrate his 60th birthday. His pioneering work has always inspired us.

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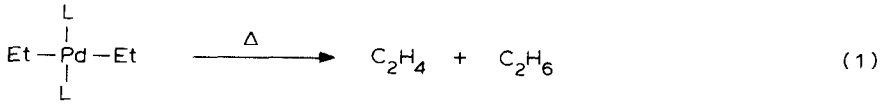
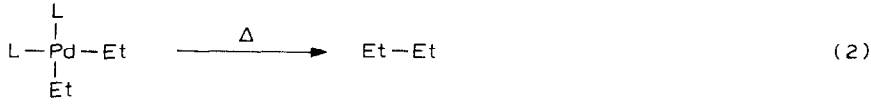
trans- and *cis*-diethylpalladium complexes having two tertiary phosphine ligands (L) [3a,4].

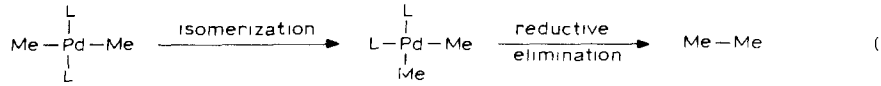


(1)



(2)

It was further demonstrated that *trans*-dimethylbis(tertiary phosphine)palladium does not give the reductive elimination product directly but has to be first isomerized to a *cis*-dimethyl complex before undergoing the reductive elimination [3a,b].

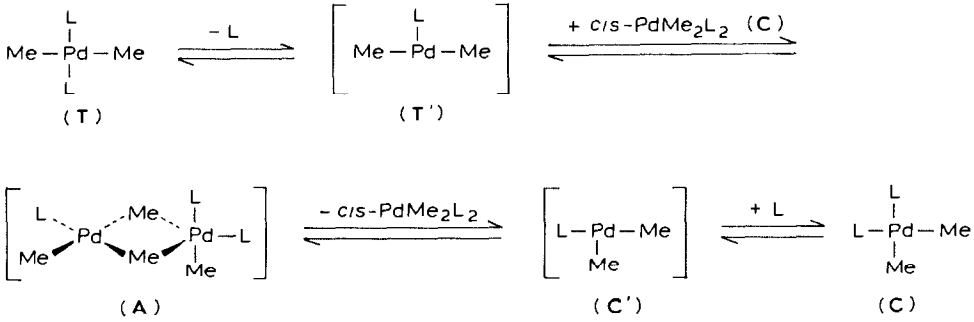


(3)

These results indicate that the two alkyl groups bonded to palladium should be brought to mutually *cis* positions for undergoing the reductive elimination to give a C–C coupling product. Therefore in order to achieve the selective C–C coupling reactions promoted by palladium compounds promotion of the *trans-cis* isomerization has a crucial importance.

The *trans-cis* isomerization of $PdMe_2L_2$ may proceed spontaneously or be assisted by other reagents. In the isomerization of *trans*-$PdMe_2L_2$ to *cis*-$PdMe_2L_2$, Stille proposed an associative isomerization mechanism assisted by solvent or added tertiary phosphines to the system [3b], while we demonstrated occurrence of a dissociative process followed by an intermolecular methyl transfer reaction as represented by Scheme 1 for the isomerization of $PdMe_2L_2$ type complexes. This isomerization process has been supported by the kinetic evidence and the results obtained from crossover experiments using perdeuterio- and nondeuteriodimethyl complexes.

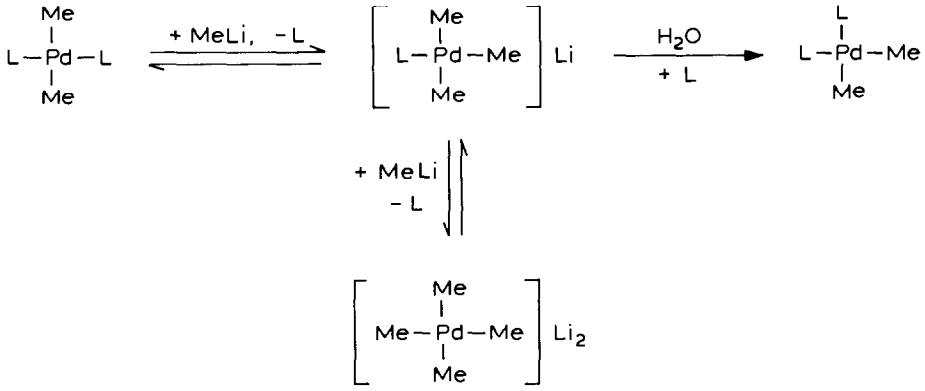
In this Scheme we assumed configurational stability of *trans* and *cis* three-coordinated species **T′** and **C′** having T-shaped geometries. This assumption is supported by theoretical treatment using extended Hückel MO calculations [5]. As the key



SCHEME 1

intermediate for the methyl transfer reaction causing *trans-cis* isomerization, the methyl-bridged complex **A** formed between the three-coordinated **T′** or **C′** and the undissociated *cis* dimethyl complex **C** was postulated. *Trans/cis* equilibrium for this reaction was found to vary with the basicity of the coordinated phosphine ligands. For the complex coordinated with less basic $PMePh_2$ and $PEtPh_2$, *trans/cis* equilibrium lies far on the side of the *cis* form in acetone or CH_2Cl_2 (*trans/cis* = 0), whereas the isomerization of the complexes having more basic ligands, PMe_2Ph, PEt_2Ph, and PEt_3, reaches the equilibria in favor of enhanced ratios of *trans* isomers in the equilibrium mixtures (*trans/cis* = 0.07 (PMe_2Ph), 0.20 (PEt_2Ph), 1.2 (PEt_3)).

The second type of *trans-cis* isomerization involves a process assisted by alkylmetal compounds of Main Group elements such as lithium and magnesium. These metal alkyl-assisted isomerization is relevant to C–C bond formation reactions between these metal alkyls and aryl or alkenyl halides promoted by palladium or nickel compounds [6,7]. In the previous report [3a] it was shown that *trans*-$PdMe_2L_2$ type complexes are readily transformed into correspoding *cis* isomers by treatment with MeLi followed by hydrolysis of the reaction systems. In this case



SCHEME 2

trans to *cis* isomerization process is irreversible independent of the coordinated tertiary phosphine ligands. NMR spectroscopic studies on the isomerization system have revealed that the process involves tri- and tetramethylpalladate complexes as the key intermediates, which are formed by the stepwise displacement of tertiary phosphine ligands (L) with MeLi. Hydrolysis of these palladate species affords *cis*-$PdMe_2L_2$, selectively [8].

We now report another type of *trans-cis* isomerization of $PdMe_2(PEt_2Ph)_2$ in tetrahydrofuran (THF) solution promoted by methylmagnesium compounds, Me_2Mg and MeMgBr. Kinetic and isotopic studies on the isomerization process have revealed the occurrence of a previously unrecognized isomerization process catalyzed by methylmagnesium compounds. The results are relevant to catalytic C–C coupling processes using Grignard reagents as a component.

Results

Before showing the results of *trans-cis* isomerization of $PdMe_2(PEt_2Ph)_2$ (*trans*, **1**; *cis*, **2**) in the system with methylmagnesium compounds, we need to describe the

behavior of the dimethyl complex in THF without methylmagnesium compounds. Although THF is a preferred solvent to dissolve methylmagnesium compounds and to study the effect of methylmagnesium compounds on isomerization of dimethylpalladium complexes by means of NMR spectroscopy, the dimethylpalladium complexes were found to undergo rapid, complicated isomerization and decomposition reactions when dissolved in neat THF without the methylmagnesium compounds. When a THF solution of **1** prepared below $-30\,^{\circ}C$ was brought to room temperature, about 50% of **1** was rapidly converted into the *cis* isomer **2** within 5 min *. Simultaneously, decomposition of the dimethyl complexes with evolution of ethane and methane proceeded and the color of the reaction solution slightly darkened. Rapid isomerization of the *cis* isomer **2** into the *trans* isomer **1** in THF was also noted. In this reverse system about 20% of **2** was spontaneously converted into **1** accompanied by decomposition of the dimethyl complexes at room temperature. After the occurrence of the rapid isomerization and decomposition at the first stage, the reaction rate became markedly slow probably due to the retardation effect of free PEt_2Ph ligand released by the decomposition of the dimethyl complex. Indeed, *trans-cis* isomerization and decomposition of **1** and **2** were effectively blocked in a system containing a small amount of PEt_2Ph (< 1 equiv./Pd). Further study on the *trans-cis* isomerization reaction in THF has not been made because the reaction rate is too fast for usual kinetic study and the thermal decomposition of the dimethyl complex cannot be ignored even at low temperature. However, the rapid isomerization and decomposition of the dimethylpalladium complexes were completely suppressed in the presence of methylmagnesium compounds and they showed well-behaved isomerization processes as shown below.

Isomerization in the presence of methylmagnesium compounds

In contrast to the very rapid isomerization and partial decomposition of the dimethyl complexes in THF without methylmagnesium, *trans* to *cis* and *cis* to *trans* isomerization reactions of $PdMe_2(PEt_2Ph)_2$ proceed in modest rates amenable to kinetic studies in THF solution containing methylmagnesium compounds such as Me_2Mg and MeMgBr.

$$\underset{(\mathbf{1})}{\textit{trans}\text{-}PdMe_2(PEt_2Ph)_2} \overset{Me_2Mg \text{ or } MeMgBr}{\rightleftharpoons} \underset{(\mathbf{2})}{\textit{cis}\text{-}PdMe_2(PEt_2Ph)_2} \qquad (4)$$

Figure 1 illustrates the typical time-conversion curves for the *trans* to *cis* and *cis* to *trans* isomerizations in THF containing 3.2 equimolar amounts of Me_2Mg at $33\,^{\circ}C$. These reaction curves were obtained by following the change in peak intensities of Pd–*Me* signals of **1** and **2** in their ^1H NMR spectra. The *trans-cis* isomerization is completely free from a thermal decomposition of the dimethyl complexes and reaches an equilibrium of *trans*/*cis* = 0.25 in 2 h.

The ^1H NMR spectra of **1** and **2** isomerized by addition of the dimethylmagnesium compounds were free of species other than **1**, **2**, dimethylmagnesium compound, and THF. Therefore formation of a palladate complex as a detectable entity as observed in the reaction of $PdMe_2L_2$ with MeLi can be excluded. It was also

* Isomerization rate in THF is much faster than that in other solvents such as toluene, acetone, and CH_2Cl_2 [3a].

confirmed that the added Me_2Mg was not consumed to give any other metal alkyls.

Table 1 shows *trans-cis* equilibrium constants of $PdMe_2(PEt_2Ph)_2$ under various conditions. Equilibrium constants are almost independent of kinds and concentrations of methylmagnesium compounds. The equilibrium was found not to be shifted by varying the temperature within the experimental error at 0, 20, and 33°C.

Trans-cis equilibrium constants were also measured for the dimethyl complexes coordinated with other three kinds of teriary phosphine ligands: PMe_2Ph, PEt_3, and $PMePh_2$. For the PMe_2Ph- and $PMePh_2$-coordinated complexes, equilibrium lies far on the side of the *cis* form, whereas PEt_3-coordinated dimethyl complex undergoes

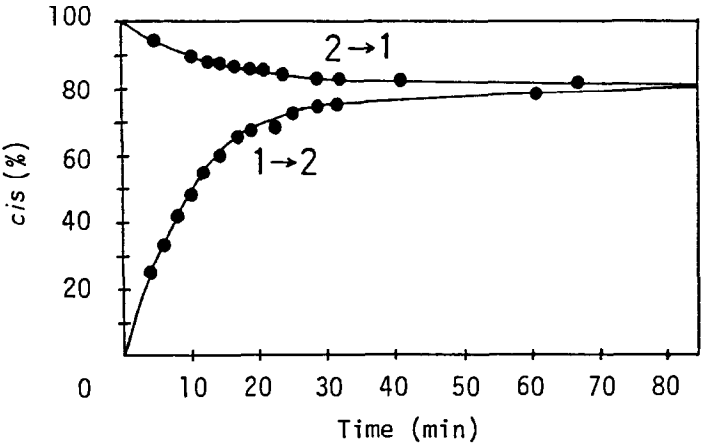


Fig. 1. Time-conversion curves of *trans-cis* isomerization of $PdMe_2(PEt_2Ph)_2$ (*trans*, **1**; *cis*, **2**) catalyzed by Me_2Mg in THF at 33°C. [$PdMe_2(PEt_2Ph)_2$] 0.1 mol l^{-1}, [Me_2Mg] 0.32 mol l^{-1}.

TABLE 1

Cis-trans EQUILIBRIUM CONSTANTS OF $PdMe_2(PEt_2Ph)_2$ IN THF IN THE PRESENCE OF METHYLMAGNESIUM COMPOUNDS UNDER VARIOUS CONDITIONS [a]

Starting compound	MeMgX (mol l^{-1})	Temp. (°C)	*trans*/*cis* ratio
cis (**2**)	Me_2Mg (0.11)	0	0.28
		20	0.28
	Me_2Mg (0.33)	0	0.23
		20	0.25
	Me_2Mg (0.88)	20	0.23
	MeMgBr (0.28)	20	0.28
trans (**1**)	Me_2Mg (0.96)	0	0.27
		20	0.25
	Me_2Mg (0.32)	33	0.25
	MeMgBr (0.21)	20	0.27

[a] [complex] = 0.1 mol l^{-1}.

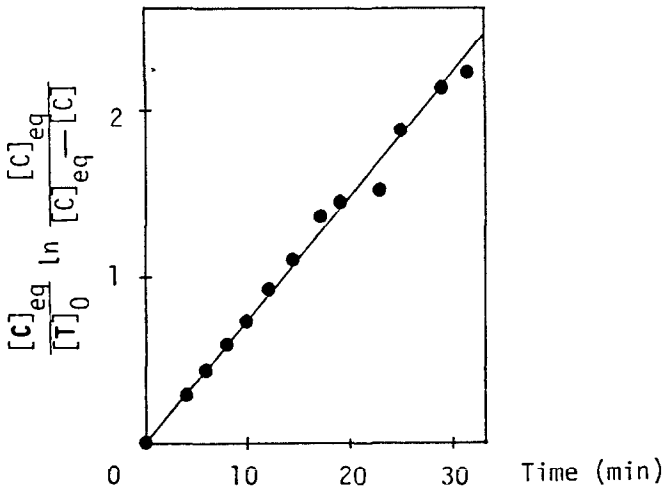


Fig. 2. Plot of $([C]_{eq}/[T]_0)\ln\{[C]_{eq}/([C]_{eq}-[C])\}$ vs. t in *trans* to *cis* isomerization of $PdMe_2(PEt_2Ph)_2$ catalyzed by Me_2Mg in THF at 33°C

trans to *cis* and *cis* to *trans* isomerization and reaches the equilibrium of *trans*/*cis* = 2.7 at room temperature. These results show that electronic factor of tertiary phosphine ligands predominantly influences the equilibrium and the coordination of more basic phosphine ligands gives the higher *trans* ratio at the equilibrium state in agreement with the results reported previously [3a] *.

Kinetics

Kinetic experiments for the isomerization reaction of $PdMe_2(PEt_2Ph)_2$ in THF containing Me_2Mg at 33°C have been made by following the time-change of relative intensity of Pd–*Me* signals in *trans* (**1**) and *cis* (**2**) isomers in ^1H NMR spectra. Since the time-conversion curves of *trans* to *cis* and *cis* to *trans* isomerization reactions given in Fig. 1 suggest that both forward and backward reactions are approximately first-order in the concentration of the dimethyl complexes, the decreasing rate of *trans* isomer may be expressed by eq. 6, where [**T**] and [**C**] are concentrations of the *trans* and *cis* isomers at the time.

$$\underset{(\mathbf{1})}{trans\text{-}PdMe_2(PEt_2Ph)_2} \underset{k'}{\overset{k}{\rightleftharpoons}} \underset{(\mathbf{2})}{cis\text{-}PdMe_2(PEt_2Ph)_2} \tag{5}$$

$$-\frac{d[\mathbf{T}]}{dt} = \frac{d[\mathbf{C}]}{dt} = k[\mathbf{T}] - k'[\mathbf{C}] \tag{6}$$

According to the conventional method for the kinetics of reversible system [11], the following rate expression is derived where $[\mathbf{T}]_0$ stands for the inital concentration of **1** and $[\mathbf{C}]_{eq}$ denotes the concentration of **2** at the equilibrium state.

$$\frac{[\mathbf{C}]_{eq}}{[\mathbf{T}]_0} \ln \frac{[\mathbf{C}]_{eq}}{[\mathbf{C}]_{eq}-[\mathbf{C}]} = kt \tag{7}$$

* Tolman's cone angle θ [9] and pK_b values [10] of tertiary phosphine ligands, which are measures of steric and electronic factors of phosphine ligands, respectively, are as follows: (θ (°), pK_b) PEt_3 (132, 5.35) PEt_2Ph (136, 7.22), PMe_2Ph (122, 7.75) $PEtPh_2$ (140, 9.09) $PMePh_2$ (136, 9.35).

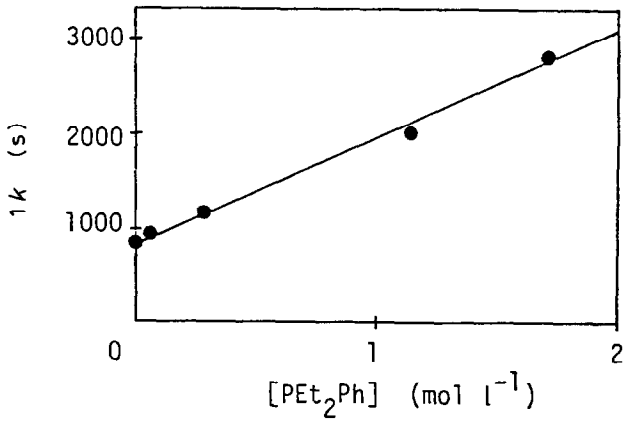


Fig. 3. Plot of $1/k$ vs. $[PEt_2Ph]$. $[Me_2Mg] = 0.32$ or 0.33 mol l^{-1}.

TABLE 2

RATE CONSTANTS (k and k') FOR THE *trans-cis* ISOMERIZATION OF $PdMe_2(PEt_2Ph)_2$ PROMOTED BY Me_2Mg [a]

Additive (mol l^{-1})		k	k'
PEt_2Ph	Me_2Mg	($\times 10^{-3}$ s^{-1})	
0.057	0.33	1.0	0.26
0.057	0.18	0.80	0.20
0.057	0.091	0.61	0.15
0.057	0.065	0.49	0.12
0.057	0.023	0.22	0.06
0	0.32	1.2	0.30
0.057	0.32	1.0	0.26
0.28	0.32	0.85	0.21
1.14	0.33	0.50	0.12
1.71	0.33	0.35	0.09

[a] In THF at 33°C. [complex] = 0.1 mol l^{-1}.

Plot of the left term vs. time t as computed from the time-conversion curve for the *trans* to *cis* isomerization shown in Fig. 1 gives a straight line as represented in Fig. 2. From the slope of the line the value of k is obtained as 1.2×10^{-3} s^{-1}. Since $k'/k = [T]_{eq}/[C]_{eq} = 0.25$, k' is calculated as 0.3×10^{-3} s^{-1}.

Table 2 lists the rate constants k and k' obtained under various reaction conditions. The forward and backward isomerization rates increase with increase in the concentration of added dimethylmagnesium, while the reaction is moderately retarded by addition of free PEt_2Ph to the system. Plotting of $1/k$ vs. $[PEt_2Ph]$, the concentration of added PEt_2Ph, gave a straight line as shown in Fig. 3. Furthermore, the $1/k$ value was found to be proportional to the reciprocal of $[Me_2Mg]$, the concentration of Me_2Mg (Fig. 4) *.

* Kinetic runs of Fig. 4 concerning the effects of addition of Me_2Mg have been performed in the presence of added PEt_2Ph ($[PEt_2Ph] = 0.057$ mol l^{-1}) in order to minimize the contribution of isomerization process proceeding without Me_2Mg.

The value of the intercept obtained by extrapolation of the line in Fig. 3 to zero concentration of PEt_2Ph is almost identical with the observed rate constant k at $[PEt_2Ph] = 0$, suggesting that the process without participation of Me_2Mg can be ignored in the system containing Me_2Mg.

Isomerization of cis-Pd(CD$_3$)$_2$(PEt$_2$Ph)$_2$ in the presence of (CH$_3$)$_2$Mg

Cis-trans isomerization of *cis*-$Pd(CD_3)_2(PEt_2Ph)_2$ in the presence of $(CH_3)_2Mg$ was followed by means of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. At the initial stage

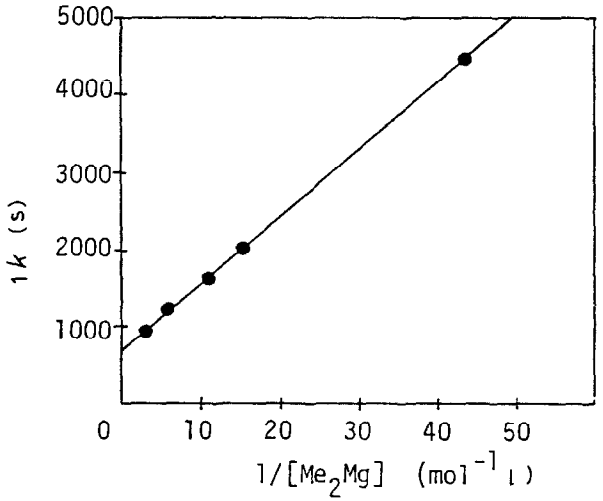


Fig. 4. Plot of $1/k$ vs. $1/[Me_2Mg]$. $[PEt_2Ph] = 0.057$ mol l^{-1}.

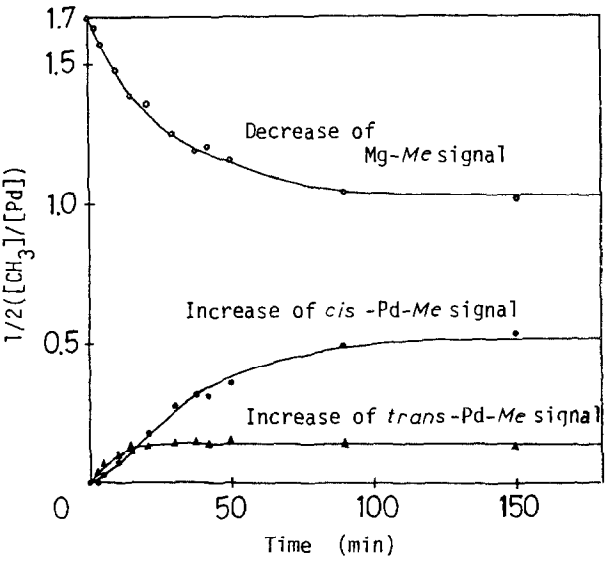


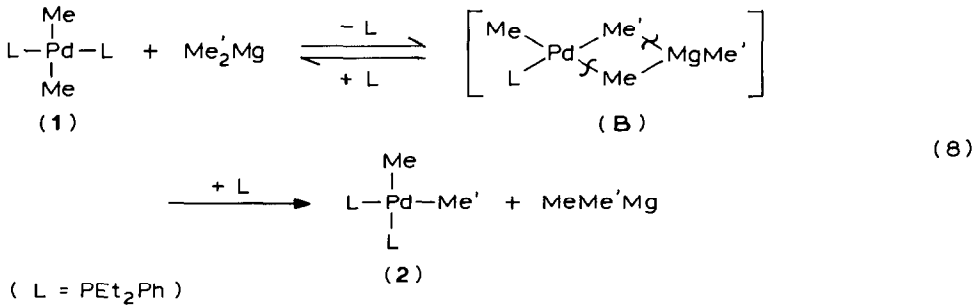
Fig. 5. Time course of relative intensity of ^1H NMR signals on the reaction of *cis*-$Pd(CH_3)_2(PEt_2Ph)_2$ with $(CH_3)_2Mg$ in THF at 33°C. ○, Mg-*Me*; ●, *cis*-Pd-*Me*; ▲, *trans*-Pd-*Me*. Initial conditions: $[(CH_3)_2Mg] = 0.19$ mol l^{-1}, [*cis*-$Pt(CD_3)_2(PEt_2Ph)_2$] = 0.11 mol l^{-1}, $[PEt_2Ph] = 0.057$ mol l^{-1}

of the reaction the ^1H NMR spectrum of the THF solution containing perdeuteriodimethylpalladium complex (0.11 mol l^{-1}), nondeuteriodimethylmagnesium (0.19 mol l^{-1}), and added PEt_2Ph (0.057 mol l^{-1}) exhibited a singlet at δ −1.75 ppm arising from the protons of Me_2Mg and no signal corresponding to Pd–*Me* protons was observed. On standing the sample solution at 33°C, *trans*- and *cis*-Pd–*Me* signals gradually appeared at δ −0.67 and +0.08 ppm, respectively, accompanied by the decrease of the signal corresponding to the dimethylmagnesium as shown in Fig. 5. At the initial period *trans*-Pd–*Me* signal predominantly increases, and that is followed by the increase of *cis*-Pd-*Me* signal, suggesting that *cis*-dimethylpalladium complex containing CH_3 group(s) is produced from *trans* isomer formed by the interaction of *cis*-CD_3-dimethylpalladium complex with $(CH_3)_2Mg$. The system reaches the equilibrium in 2.5 h (*cis*-Pd–CH_3/*trans*-Pd–CH_3/Mg–CH_3 = 4/1/8). At this time, $^{31}P\{^1H\}$ NMR spectrum of the solution also showed that the system reached the *trans-cis* equilibrium. The equilibrium ratio of CH_3 signals of these three components indicates the occurrence of complete scrambling of the methyl groups. The rate of decrease of Mg–CH_3 protons is comparable to the rate of *cis* to *trans* isomerization of dimethylpalladium complex as judged from the decreasing curve of Mg–CH_3 protons in Fig. 5 and the time-conversion curve for the *cis* to *trans* isomerization of $PdMe_2(PEt_2Ph)_2$ measured under same reaction conditions. These results strongly suggest that the *cis-trans* isomerization reaction proceeds through intermolecular methyl transfer reaction between the dimethylpalladium complex and Me_2Mg. Intermolecular exchange of the methyl groups was also observed between *cis*-$Pd(CD_3)_2(PEt_2Ph)_2$ and CH_3MgBr.

Discussion

The above experimental results strongly suggest that methylmagnesium compounds are involved in the methylmagnesium-catalyzed isomerization through participation in the intermolecular methyl exchange process and that a dissociation of PEt_2Ph ligand should be involved in the isomerization mechanism.

We first consider the *trans* to *cis* isomerization mechanism of $PdMe_2(PEt_2Ph)_2$ catalyzed by Me_2Mg. As a likely intermediate responsible for the interconversion of the *trans* complex to the *cis* isomer involving the methyl exchange process, we postulate the following binuclear species B bridging between Pd and Mg through two methyl groups.



(8)

Similar intermolecular transfer processes of anionic ligands such as Me and Cl through a bimolecular intermediate bridged by two anionic groups has been pro-

posed for the disproportionation [12] and isomerization [13] reactions of d^8 square planar transition metal complexes.

Two types of mechanisms are conceivable for formation of intermediate **B**. Direct attack of dimethylmagnesium on four-coordinate *trans* complex **1** will form the intermediate **B** accompanied by dissociation of the PEt_2Ph ligand (L). An alternative process involves a prior dissociation of L from **1** to form the three-coordinate species, *trans*-$PdMe_2L$ (**T'**), having a T-shaped geometry. In this case reaction of **T'** with dimethylmagnesium gives the bridged intermediate **B**.

Cleavage of the original methyl–palladium and –magnesium bonds in **B** may liberate three-coordinate *cis*-dimethylpalladium (**C'**) having a T-shaped structure and dimethylmagnesium with concomitant exchange of the methyl groups between Pd and Mg. Coordination of L to **C'** completes the *trans* to *cis* isomerization, giving *cis*-$PdMe_2L_2$ (**2**). Alternatively, associative cleavage of the orginal methyl–palladium and –magnesium bonds in **B** by PEt_2Ph ligand will give complex **2** with regeneration of dimethylmagnesium. From the presently available data it is hard to decide which types of processes are operative in the formation and breaking up reactions of intermediate **B**.

The *cis* to *trans* isomerization will proceed through the reversal process of eq. 8. In this case liberation of Me_2Mg from **B** formed by the interaction of *cis*-dimethylpalladium complex **2** and Me_2Mg gives *trans*-dimethylpalladium complex accompanied by coordination of L.

Although alkylmagnesium compounds are usually employed in excess amounts as reagents for cross coupling reactions with organic halides catalyzed by palladium compounds [6], little attention has been paid so far to the possible effect of alkylmagnesium compounds on the behavior of diorganopalladium species in the currently accepted reaction mechanisms. The observations in the present study indicate that the role of alkylmagnesium compounds is not restricted to that of the alkylating agent and promotion effect of the isomerization of the intermediate diorganopalladium compounds to induce the C–C coupling reactions should not be overlooked.

Experimental

All manipulations were carried out under nitrogen or argon atmosphere. Solvents were dried and distilled by conventional methods and stored under argon atmosphere. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL PS-100 and FX-100 spectrometers. Chemical shifts in ^1H NMR spectra are referred to Me_4Si as an external standard. *Trans*- and *cis*-$PdMe_2L_2$ complexes (L = PEt_3, PMe_2Ph, PEt_2Ph, and $PMePh_2$) were prepared according to the methods described previously [3a].

Dimethylmagnesium was initially prepared as an Et_2O solution of dioxane adduct $Me_2Mg(dioxane)_{0.5}$ from methylmagnesium bromide and dioxane by the literature method. After removal of Et_2O by pumping, the resulting white solid of Me_2Mg was dissolved into dry THF and stored under an argon atmosphere. Concentration of Me_2Mg in THF solution was determined by means of ^1H NMR spectroscopy using dry benzene as an internal standard.

Studies of trans-cis isomerization of dimethylpalladium complexes

To a Schlenk tube containing an adequate amount of *trans*- or *cis*-dimethylpal-

ladium complex (~ 0.1 mmol) and/or tertiary phosphine, an appropriate quantity of a THF solution of Me_2Mg or MeMgBr and dry THF (totally 1 ml) was added by means of a measuring pipette. The sample solution was replaced into an NMR sample tube below $-30\,^{\circ}C$. The sealed tube was placed in a thermostatted NMR probe ($\pm 1.0\,^{\circ}C$). The amounts of *trans* and *cis* isomers on isomerization with time were followed by measuring the ratio of the areas of Pd–*Me* signals of both isomers.

The *trans-cis* equilibrium ratio was determined by measuring the relative intensity of Pd–*Me* signals of *trans* and *cis* isomers in ^1H NMR spectra after allowing the sample in a thermostatted bath at least for a day. The *trans-cis* ratio at an equilibrium state was also confirmed by $^{31}P\{^1H\}$ NMR spectroscopy.

Acknowledgement

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